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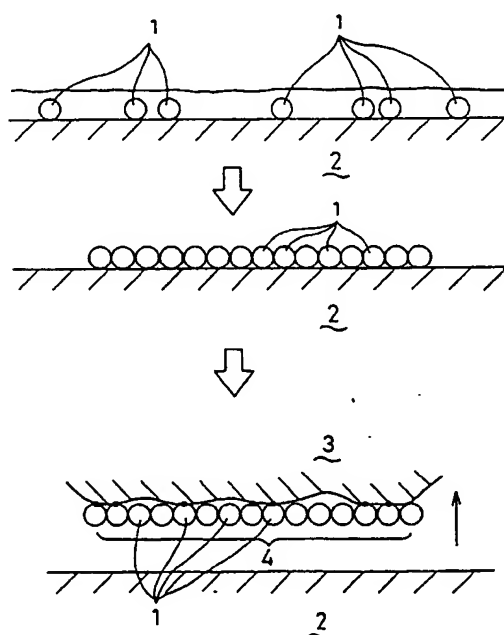
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**A method for forming a thin two-dimensional particulate coating.**

Particle-containing or particle-forming liquid is spread over the surface of a high density liquid; the particles are aggregated two-dimensionally by reducing the thickness of the particle-containing or particle-forming liquid; and the aggregated and thin two-dimensional particulate film formed is brought into contact with the surface of a solid substrate to transfer and fix said thin film thereon.

The two-dimensional aggregation can take place to form thin films of high quality.

*Fig. 1*



The present invention relates to a method for forming a thin two-dimensional particulate film and in particular to a new method for forming such films which is useful for production of new functional materials for use in various fields including electronics and bio-materials.

Fine particles and thin films thereof have long been considered promising new materials for realising new and high level functions in the fields of electronics and bio-materials, and methods of forming thin films from fine particles have been actively studied. Various methods are known and they are classified into two types according to the substrates used. One type uses the surface of a solid as the substrate and the other uses the surface of a liquid.

Methods using solid surfaces for spreading the particles include, for example, the drying method (wherein a particle-containing solution is put on a solid substrate such as glass, which is placed horizontally to form a thin film thereon by a drying process), the spin coat method (wherein a particle-containing solution is coated on a solid substrate), a combination of the spin coat and the drying methods, and the adsorption method, wherein glass or an other substrate is slowly immersed into a particle-containing liquid perpendicularly and the particles absorbed are fixed on the surface of the substrate.

Methods of using liquid surfaces as the substrate on which particles are spread include, for example, the most extensively applied and commonly used LB film method wherein the particles are arrayed on the interface between water and air and are transferred to a secondary solid substrate via physical concentration such as compression.

However, it is not easy to form thin two-dimensional particulate film of high quality at high efficiency and to control the formation of the structure or its organisation. Indeed, the attempt to apply these methods to fine practices has major drawbacks.

The most serious problems of the conventional methods include, for example, (1) nonuniform particle placement, (2) very low thin film forming speed, (3) difficulty of formation and control of a single layer of particles, and (4) difficulty of application of the method to fine particles of the order of a nanometre in size.

The reasons why these problems are unavoidable include: (1) nonuniform particle placement is unavoidable because of, mainly, poor flatness of the surface, and (2) low crystal-like or crystalline thin film formation speed is due to low level of cleanliness of the solid and liquid substrate surfaces. Poor flatness and low level of cleanliness of the substrate surface decrease the power of the particles to aggregate, and thus only incomplete films of low density are produced.

Further, the problems of (3) difficulty of formation and control of a single particle layer and (4) difficulty of application of the method to fine particles

having sizes of the order of a nanometre have not been solved because there has been no means to evaluate the force applied to individual particles.

The present invention has been made in consideration of the above situation, solves the problems of the prior art and provides a new method of controlling the aggregation of particles, thereby forming a high quality uniform thin two-dimensional film of particles at high efficiency.

## SUMMARY OF THE INVENTION

The invention provides a method for forming a thin two-dimensional particulate film comprising the steps of spreading a particle-containing or particle-forming liquid onto the surface of a high density liquid, reducing the thickness of said particle-containing or particle-forming liquid to form a two-dimensional assembly of particles on the surface of the liquid, contacting a solid substrate with the thin two-dimensional particulate film formed, and transferring the thin film to the surface of a solid substrate by fixation of the thin particle film to the surface of solid substrate.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram illustrating the method of the invention.

Figures 2 and 3 are sectional diagrams illustrating the mechanism of aggregation of particles in the invention.

Figures 4-6 are electron micrographs of the products of the examples.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to Figure 1, liquid containing particles (1), or capable of forming particles, is spread on the surface of a high density liquid (2) serving as the primary substrate. The thickness of said liquid is reduced for example by evaporation or suction of the liquid. The two-dimensional aggregation of particles is promoted by flow force, for example, resulting from this control. The high density liquid (2) is flatter and cleaner than conventional substrates that suffer from poor flatness and poor cleanliness, and behaves like a solid substrate, resulting in substantial cohesion of the particles (1) via uniform lateral liquid immersion force, laminar flow force, etc.

With the present invention, further, it is possible to transfer particles (1) aggregated on the high density liquid (2) to the surface of a solid substrate (3) serving as the secondary substrate and fix the thin two-dimensional crystal-like or crystalline film (4) of fine particles thereon. In this way, thin film fixation is possible.

The high density liquid (2) used in the present in-

vention may be, for example, mercury, gallium or any other liquid metal that will not allow penetration of the particles (1) and liquid. The solid substrate serving as the secondary substrate may be, for example, a carbon substrate, LB film substrate, glass substrate, synthetic high molecular weight substrate, natural high molecular weight substrate, mica or any other inorganic substrate. These solid substrates (2) are selected according to the affinity required for the transfer and fixation of particles (1).

The particles used may be made of synthetic or natural resins, inorganic, metallic, or other substances. They may be dispersed in water or an organic solvent or may be formed by precipitation from a solution.

The thickness of the liquid film is controlled by, for example, evaporating the liquid containing the particles or by controlling the liquid pressure in order to aggregate the particles two-dimensionally. In this case, cohesion is induced and becomes effective when the liquid thickness is reduced to or below the diameter of the particles making it possible to control the aggregation speed, and form a thin two-dimensional particulate film in which the size of the aggregated material is controlled. When the particle diameter is nonuniform, the aggregation density of the larger particles is faster than that of the smaller particles. By using this phenomenon, it is possible, for example, to form these with particles of larger diameter at the centre and particles of smaller diameter around the centre or around the larger particles.

The powerful and fast two-dimensional aggregation process for the formation of thin films is further described below. The aggregation process of the invention essentially comprises two processes, core formation and crystal-like growth processes.

These are many factors in the core formation process. The lateral liquid immersion force has been studied by the present inventor and is discussed below.

As shown in Figure 2, particles A and B dispersed in liquid I are spread over substrate III having a flat surface and the thickness  $d$  of liquid I is reduced down to approximately the diameter of particles A and B, particularly to lower than the diameter of the particles. This causes a large suctional force  $F$  to act on particles A and B to form a two dimensional core of aggregated particles.

It is theoretically predicted that the lateral liquid immersion force acting as suctional force  $F$  varies with the contact angle between the particle and liquid I, the thickness  $d$  of liquid I at a point remote from the particles, the diameter  $2r$  of particles A and B, the interfacial tension between liquid I and medium II (surface tension if the liquid I is air), and the difference in density between liquid I and medium II. The lateral liquid immersion force is effective over a long distance and is proportional to the inverse of distance 1 be-

tween the particles. The attraction is at work between the particles which are significantly far apart because the lateral liquid immersion force is effective over such long distances.

The more wettable the particles are to the liquid dispersion medium, the greater the attraction, and the faster the two-dimensional aggregation which forms the crystal-like cores.

As described above, core assemble of particles is formed at a certain point on a substrate having a flat surface mainly owing to the attraction between particles and lateral liquid immersion force.

Aggregation of particles in the crystal-like growth process also depends on the laminar flow occurring in the particle liquid I as a result of evaporation, etc., as shown in Figure 3. The attraction between particles and the lateral liquid immersion force is also at work in the crystal-like growth process.

That is, evaporation increases near the core area 10, which was formed in the above core formation process, when liquid I is evaporated, and the liquid thickness is reduced to about the same size as the particles. The liquid around the core area 10 flows into the core in an attempt to keep the liquid thickness uniform, thereby creating laminar flow in the liquid. Speed distribution ( $\alpha$ ) of the laminar flow force is largest near the surface of the liquid, owing to the friction with the substrate III, and decreases as the flow approaches the substrate. For this reason, a speed gradient is produced in the liquid and a rotating force ( $\beta$ ) is induced in particles C. The particles are aggregated around core area as they are rolled on the substrate under rotating force ( $\beta$ ) and parallel forwarding force ( $\gamma$ ). The rotating force ( $\beta$ ) and parallel forwarding force ( $\gamma$ ) work as a force to separate the particles off the substrate III when the particles are adhered to substrate III, thereby promoting smooth two-dimensional aggregation or forming an excellent two-dimensional assembly. The laminar flow in liquid I, resulting from evaporation, has a limiting thickness, which is estimated at approximately 1 mm below the surface. Accordingly, the size of the particle should preferably be 1 mm or less in the present invention.

The thin two-dimensional particle film on the surface of high density liquid is then fixed to the surface of solid substrate.

The fixation of the thin film to the surface of solid substrate depends on physical or physico-chemical absorption forces or linkage force between the particles of the thin film and the surface of solid substrate. It is preferable for the fixation to use a solid substrate having a larger surface active force, such as a carbon surface.

It is possible to produce uniform solid thin films by melting and sintering the thin two-dimensional particle film produced by the fixation process above-mentioned. When this solid thin film is used in optics, for example, it is possible to produce high precision

optical reflection filters, photographic lenses, copy lenses, glare preventive films and other sold film, etc.

Further, the thin films can be fixed as individual patterns, or converted into film structures of excellent functionality by chemically modifying the film or processing, and by modifying or otherwise treating the film by light, e.g. with a laser. It is also possible to make multilayered films from single layer films. It is also possible to apply the method to the production of new functional materials to be used in various industrial fields such as electronics, bio-materials, ceramics, and metals.

Regarding the substrate, it is preferable to use mercury or liquid gallium as the high density liquid and to use a carbon solid substrate or film thereof, OB film, glass plate substrate, synthetic high molecular weight substrate, natural high molecular weight substrate, or an inorganic substrate as a solid substrate.

The liquid above mentioned is preferably water or an alcohol, ether, ester, hydrocarbon, or other organic medium or mixture thereof. There is no limitation regarding to the kinds of particles and the size of thereof.

Various kinds of organic particles may be used. Inorganic particles or metal particles may be also used.

High molecular polymer materials, such as polystyrene, polyvinylchloride, polyester, polydiene, styrene-butadiene copolymer, and acrylic acid ester-maleic acid ester copolymer, may for example be used as the particles.

Inorganic materials, such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiN}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ ,  $\text{BaTiO}_3$ , and metals, such as Ti, Ni, Al, Zr, Cu, Ti-Ni alloy, Ni-Cr alloy, Cr-Mo alloy, Au, Ag, Pd and Pt may also be used for the particles.

The particle may have a size from the order of a nanometre to the order of a millimetre. The nanometre size of particles is preferably used.

The present invention is described in more detail in the examples below.

#### Example 1

A thin two-dimensional particle film was produced using the method of the present invention.

Mercury was used as the high density liquid serving as the primary flat substrate. A 20 nm thick carbon thin film on a glass plate was used as the solid substrate serving as the secondary substrate for fixing the thin film.

A small quantity of ferritin particles of approximately 12 nm particle size dispersed in water was formed over a clean mercury surface.

The water was then evaporated to reduce the thickness of the liquid. Formation of the core crystal-like aggregation occurred when the liquid thickness was 0.09m. Immediately after the formation of the core area of particles, certain particles are started to

aggregate quickly and formed a densely packed two-dimensional single particle layer.

A 20 nm thick carbon film serving as the secondary solid substrate was then brought into direct contact with the two-dimensional particle layer for transfer and fixation. The particle layer is fixed on the surface of the solid by physical absorption or adhesion. Figure 4 is an electromicrograph of the thin two-dimensional film of crystal-like ferritin particle film thus transferred.

In this way, a thin film of the densely packed two-dimensional aggregate of nanometre-sized particles was formed on a solid substrate.

#### Example 2

In like manner as Example 1, a small quantity of a mixture of polystyrene particles of approximately 55 nm and 144 nm particle sizes dispersed in water was spread over a clean mercury surface. A thin two-dimensional crystal film was formed from these particles.

The water was then evaporated to reduce the thickness of liquid. Formation of core crystal-like assembly occurred when the liquid thickness was 1.20 m. Immediately after the formation of the core assembly, polystyrene particles started to aggregate quickly and formed a densely packed two-dimensional single particle layer.

Figure 5 is an electromicrograph of the thin crystal-like particle film of polystyrene particles thus transferred and fixed on the thin carbon film substrate. Figure 5 clearly shows that polystyrene particles of 144 nm particle size have flocculated at the centre and polystyrene particles of 55 nm particle size at the periphery.

#### Example 3

Polystyrene particles of 55 nm particle size only were used as in Example 2 to transfer and to fix a thin two-dimensional particle film to a thin carbon film substrate.

Figure 6 is the relevant electromicrograph.

As described in detail above, it is possible with the method by using a high density liquid as primary substrate to realize a perfectly flat surface and a clean surface free from dust, oxide film, etc. Thus, it is possible with the present invention by using the high density liquid and the solid secondary substrate for transfer of particles thin film to fix or immobilise the thin film.

Furthermore, it is possible with the present invention, by using the lateral liquid immersion force and laminar flow force, to realize a high level of two-dimensional particle aggregation in a fine controlled state.

For these reasons, it is possible to form high qual-

ity thin two-dimensional particle films quickly by using the method of the present invention.

## Claims

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1. A method for forming a thin two-dimensional particulate film comprising the steps of spreading a particle-containing or particle-forming liquid onto the surface of a high density liquid, reducing the thickness of said particle-containing or particle-forming liquid to form a two-dimensional aggregation of the particles on the surface of the liquid, contacting a solid substrate with the thin two-dimensional particulate film formed, and transferring the thin film to the surface of a solid substrate by fixation of the particles to the surface. 10 15
2. A method as claimed in claim 1 wherein said high density liquid is a liquid metal. 20
3. A method as claimed in claim 1, wherein said high density liquid is mercury or liquid gallium and said solid substrate is selected from groups of a carbon substrate, LB film substrate, glass substrate, synthetic high molecular weight substrate, natural high molecular weight substrate or an inorganic substrate. 25
4. A method as claimed in any preceding claim wherein the film is subsequently consolidated by melting and sintering or by other methods. 30

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*Fig. 1*

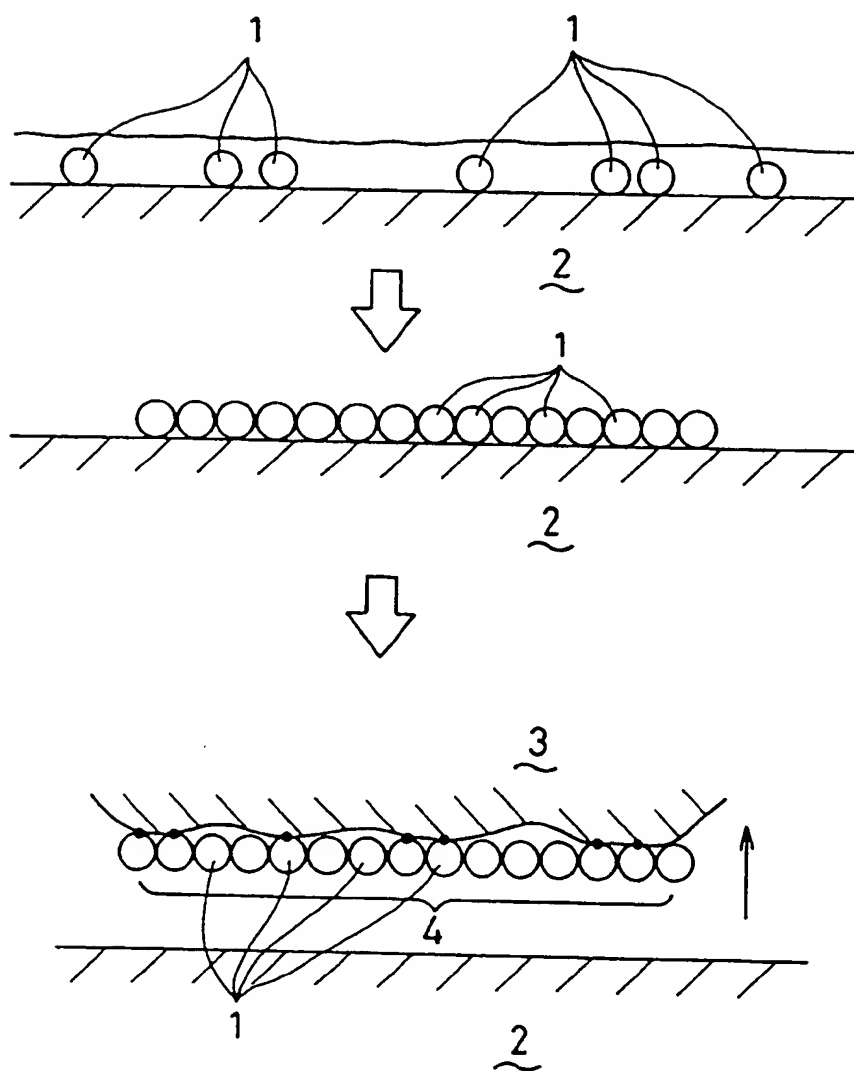
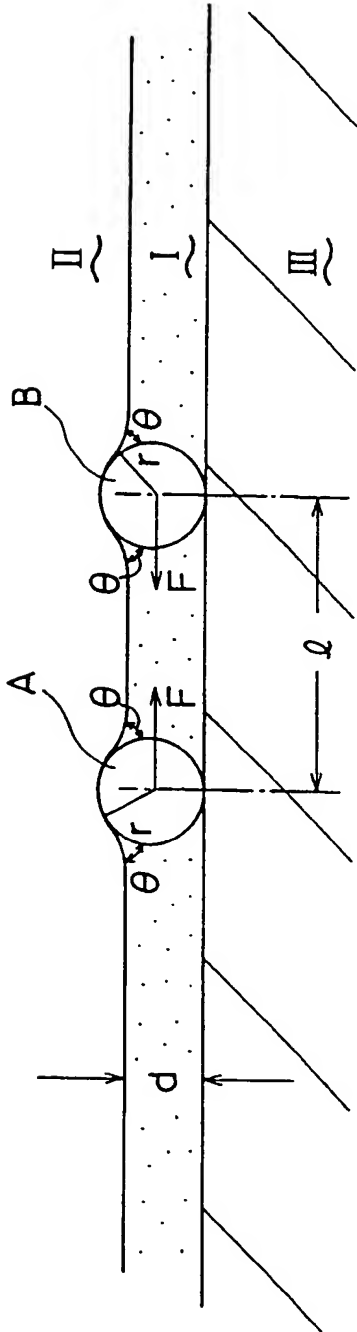
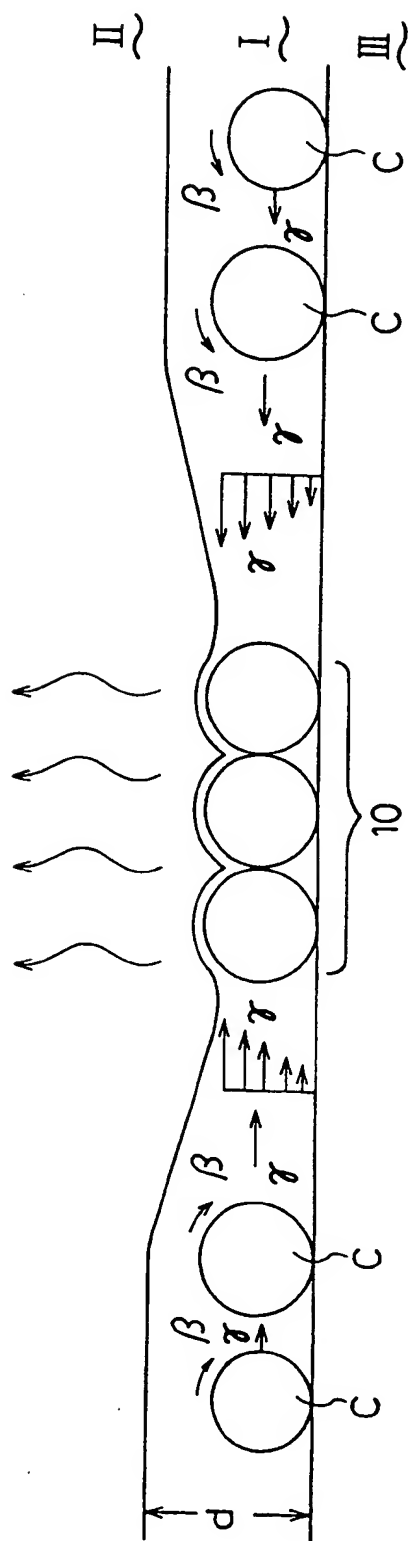


Fig. 2

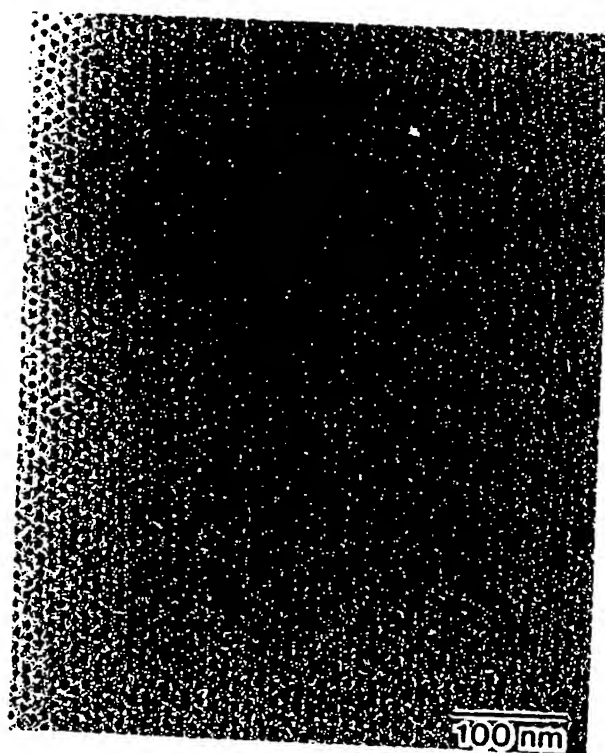




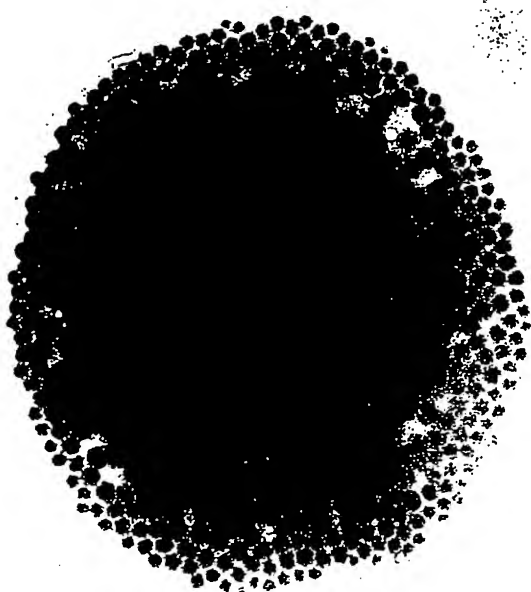
F i g. 3



*Fig. 4*

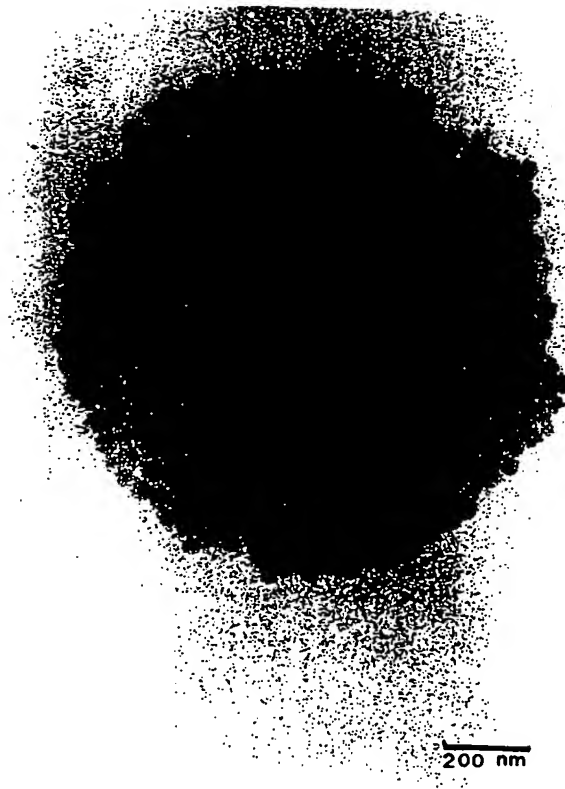


*Fig. 5*



200 nm

*Fig. 6*





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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 8545

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	EP-A-0 270 212 (EXXON RESEARCH AND ENGINEERING CO.) * the whole document *	1,4	B05D1/20
X	EP-A-0 197 461 (RESEARCH DEVELOPMENT OF JAPAN) * claim 9 *	1	
P,A	EP-A-0 541 401 (RESEARCH DEVELOPMENT CORP. OG JAPAN) * the whole document *	1	
A	US-A-2 776 908 (H.M.SMITH) * column 3, line 13 - line 17 *	4	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			B05D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 February 1994	Examiner Brothier, J-A
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